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Sol–gel electrochromic coatings and devices: A review

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Abstract

A brief updated review is made on sol–gel-derived electrochromic films (some of which used as ion storage films) of different chemical systems. Performances of selected films measured in electrochemical cells or in devices are discussed and the degradation problems experienced by different authors enumerated.

Keywords: Sol–gel; Electrochromism; Oxides

1. Introduction

Electrochromic (EC) are composed of several elements assembled in a layered configuration and are continuing to attract the attention of researchers since about the last three decades. Originally considered as an alternative to liquid crystal display devices (LCD), EC devices are now instead better set for use in daylight management, solar heat gain control [1,2] and are candidates e.g. for energy-efficient glazing in buildings, sunroofs in automobiles and automotive mirrors [3–5]. The basic function of an EC device is to exhibit repeated coloration/bleaching cycles with back and forth sweeps of small voltages.

Obviously, one of the layers in an EC device is an electrochromic film. This is accompanied by an ion storage (IS) film which can also show an electrochromic behavior, the two being placed on each sides of a solid (or liquid) electrolyte layer (E). These are the three elements of an EC device on which most of the scientific research is

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presently going on in addition to developments in device designs. The EC and IS layers, which are generally thin films of amorphous or crystalline oxides deposited on transparent conducting oxide (TCO) coated glass or plastic sheets, are prepared by a variety of standard techniques [6]. Because of the inexpensive deposition equipment and a wide choice of precursors, the sol–gel method has become a popular means among researchers for producing EC and IS films [5,7,8], as also gel-derived electrolytes [9,10].

The central idea of this article is to review as an update on previous endeavors [5,7,8], the current progress in the precursors chemistry, their utilization in the deposition of EC and IS films by sol–gel coating techniques, and the quality of such films in EC cells or devices fabricated therefrom. In addition, brief discussions are also presented on the durability and reliability issues of such EC devices.

2. Basic principles of sol–gel chemistry

The sol–gel deposition of electrochromic oxide layers has gained more and more attention during the past decade [5]. A large variety of molecular precursors are now commercially available. Many wet chemistry methods have been developed for the synthesis and deposition of electrochromic layers. Large coatings can be deposited by techniques such as spin-coating, dip-coating or spray process. With this technique molecular precursors are transformed into an oxide network by hydrolysis and condensation reactions. Two routes are currently used depending on the nature of molecular precursors: metal alkoxides in organic solvents or metal salts in aqueous solutions.

2.1. Alkoxide precursors in organic solvents

The sol–gel synthesis of metal oxides is based on the polycondensation of metal alkoxides $M(OR)_z$ in which R is usually an alkyl group ($R = CH_3$, C_2H_5,...) and z the oxidation state of the metal atom M^{z+}. The chemistry of metal alkoxides has been extensively studied during the past 30 years [11]. They can be synthesized via the reaction of metal chlorides with alcohol as follows:

$$MCl_z + zROH \Rightarrow M(OR)_z + zHCl. \quad (1)$$

The chemical reactivity of metal chlorides toward alcohol decreases with the electronegativity of the metal. Therefore most transition metal chlorides undergo only partial alcoholysis and the reaction has to be driven to completion by adding a base such as ammonia. NH_4Cl precipitates from the solution and can be removed by filtration.

Most alkoxides (M = W, V, Nb, Ti...) used for electrochromic materials are now commercially available and the sol–gel chemistry involves two steps:

(i) hydrolysis for the formation of reactive M–OH groups

$$M\text{–}OR + H_2O \Rightarrow M\text{–}OH + ROH. \quad (2)$$

(ii) and condensation leading to the formation of bridging oxygen

$$M\text{–}OH + RO\text{–}M \Rightarrow M\text{–}O\text{–}M + ROH \quad (3)$$

or

$$M\text{–}OH + HO\text{–}M \Rightarrow M\text{–}O\text{–}M + H_2O. \quad (4)$$

Metal alkoxides are not miscible with water and have to be dissolved in a co-solvent, currently the parent alcohol, prior to hydrolysis.

The chemical reactivity of metal alkoxides toward hydrolysis mainly depends on the electronegativity of the metal atom and its ability to increase its coordination number "*N*", i.e. on its size. As a general rule it increases when going down the periodic table. Niobium alkoxides for instance are much more sensitive to water than vanadium alkoxides. Coordination expansion is a general tendency of transition metal alkoxides $M(OR)_z$. It may occur via oligomerization and the molecular complexity of metal alkoxides depends on parameters such as concentration, temperature, nature of the solvent, oxidation state of the metal atom or the steric hindrance of alkoxide groups. The chemical reactivity of a given metal alkoxide $M(OR)_z$ decreases when its molecular complexity increases. This is why $Ti(OBu^n)_4$ is often used as a precursor for TiO_2 films. The Bu^n group is the largest one that does not prevent oligomerization. Oligomerization can be prevented by solvation in a polar solvent or by steric hindrance with bulky alkoxy ligands. Titanium ethoxide for instance gives $[Ti(OEt)_4]_n$ oligomers ($n \approx 4$) whereas titanium iso-propoxide $Ti(OPr^i)_4$ remains monomeric [11].

Transition metal alkoxides are usually highly reactive toward hydrolysis and have to be handled under anhydrous conditions. Therefore alkoxide solutions often have to be stabilized in order to avoid uncontrolled precipitation during the deposition process. This can be conveniently performed via chemical modification or complexation [12]. Metal alkoxides react with many hydroxylated compounds XOH such as carboxylic acids or β-diketones to form complexes as follows:

$$M(OR)_z + xXOH \Leftrightarrow M(OR)_{z-x}(OX)_x + xROH. \quad (5)$$

These reagents behave as bidentate (bridging or chelating) ligands increasing the coordination number N of the metal. They are more strongly bonded and less hydrolyzable than the alkoxy groups. The new precursors therefore exhibit a higher metal coordination and a reduced functionality. Their chemical reactivity is strongly modified and complexed alkoxides are much less sensitive toward hydrolysis and condensation.

2.2. Inorganic precursors in aqueous solutions

Transition metal alkoxides in alcoholic solutions offer several advantages as precursors for electrochromic layers. They exhibit good glass wetting and multi-component films can be easily obtained by mixing several alkoxides in the same solvent. However they may be quite expensive and highly reactive. Therefore aqueous precursors could be more appropriate for industrial applications and many papers report on

the sol–gel synthesis of electrochromic layers from aqueous solutions of transition metal salts.

When dissolved in an aqueous solution transition metal cations are solvated by dipolar water molecules giving $[M(OH_2)_n]^{z+}$ species. However H_2O is a Lewis base and the formation of $M–OH_2$ bonds draws electrons away from the bonding σ molecular orbital of the water molecule. This electron transfer weakens the O–H bonds and the coordinated water molecules behave as stronger acids than the solvent water molecules. Spontaneous deprotonation then occurs as follows:

$$[M(OH_2)_n]^{z+} + hH_2O \Leftrightarrow [M(OH)_h(OH_2)_{n-h}]^{(z-h)+} + hH_3O^+. \quad (6)$$

The hydrolysis ratio "h" corresponds to the number of protons that have been removed from the solvation sphere of the aquo-cation [13]. According to Eq. (6), h increases with the pH of the solution and the oxidation state of the metal cation M^{z+}. This leads to a whole set of aqueous species ranging from aquo-cations $[M(OH_2)_n]^{z+}$ $(h = 0)$ to neutral hydroxides $[M(OH)_z]^0$ $(h = z)$ or even oxo-anions $[MO_{n'}]^{(2n''-z)-}$ when all protons have been removed from the coordination sphere of the metal cation.

As for metal alkoxides, condensation reactions in aqueous solutions occur when at least one M–OH group is present in the hydrolyzed precursor. Condensation is usually initiated via pH modification, by adding a base to aquo-cations $[M(OH_2)_n]^{z+}$ $(z < 4)$ or an acid to oxy-anions $[MO_{n'}]^{(2n'-z)-}$ $(z > 4)$. Condensed species leading to precipitates or gels are obtained around the point of zero charge (PZC) where neutral precursors $[M(OH)_z]^0$ are formed. Less condensed molecular species known as polyanions or polycations can be formed above or below this pH [14].

Two main mechanisms are responsible for condensation:

(i) Olation with the formation of an "ol" bridge and the departure of one molecule of water.

$$-M–OH + H_2O–M- \Rightarrow -M–OH–M- + H_2O. \quad (7)$$

(ii) Oxolation involving the condensation of two OH groups to form one water molecule which is then removed giving rise to an "oxo" bridge.

$$-M-OH + HO-M- \Rightarrow -M-O-M- + H_2O. \quad (8)$$

Olation reactions occur mainly for cations of low oxidation state ($z4$) in aquo-hydroxo precursors whereas oxolation is mainly observed with cations of high oxidation state $(z > 4)$.

For a given cation, many different molecular species can be found in aqueous solutions depending on pH and concentration. They have been extensively described in several books or review papers [14].

Condensation around the PZC leads to the formation of oxides or hydroxides. These condensation reactions may be rather fast and difficult to control leading to the precipitation of coarse powders that are not suitable for the deposition of transparent coatings. As for metal alkoxides, stable solutions can be obtained via the complexation of aqueous precursors by bidentate ligands such as carboxylic acids. However,

the most convenient ligand in aqueous solutions is undoubtedly the peroxo ion $[O_2]^{2-}$ and peroxo complexes of transition metal cations have been currently used as precursors for the preparation of sols for deposition of electrochromic layers. They can be easily obtained via the dissolution of a metal powder or compound (oxide, carbide) in an aqueous solution of hydrogen peroxide H_2O_2 [15]. The peroxo group behaves as a chelating ligand. It decreases the functionality of aqueous precursors toward condensation and prevents precipitation. Peroxo complexes can then be easily decomposed upon drying around 100°C or even by dipping a platinum net into the solution [15].

3. Sol–gel synthesis of electrochromic metal oxides

3.1. Hexavalent oxides, WO_3 and MoO_3

WO_3 is by far the most studied electrochromic material and is considered the best for EC applications. It can be synthesized via many different routes using alkoxides or aqueous solutions.

Tungsten ethoxide $W(OEt)_6$ solutions stabilized by acetic acid have been used to form WO_3 layers [16,17]. However they are expensive and their high sensitivity toward water limits their utilization for commercial production [18–20].

Chloro-alkoxides appear to be more convenient precursors [21–24]. $WOCl_4$ readily dissolves in all kinds of alcohols forming stable solutions of oxychloroalkoxides.

$$WOCl_4 + x\mathrm{ROH} \Rightarrow WOCl_{4-x}(OR)_x + x\mathrm{HCl}. \quad (9)$$

This process is cheap and precursor solutions remain stable for several months. The viscosity of the solution and therefore the thickness of the coatings may be controlled with the nature of the alcohol and the concentration of the solution. WCl_6 can also be used for this purpose but it is more reactive and partially reduced by organic solvents giving blue solutions that contain W^{5+} species [25].

Many papers describe the formation of WO_3 sols from aqueous solutions [26,27]. Such sols can be easily prepared via the acidification of sodium tungstate aqueous solutions around the PZC. Acidification can advantageously be made through a proton exchange resin [28]. A clear solution is obtained that can be deposited and dried at room temperature to give amorphous $WO_3 \cdot nH_2O$ coatings. However aqueous sols are not stable. At room temperature precipitation occurs within a few days ($[W] = 10^{-2}$ M) or even hours ($[W] \approx 10^{-1}$ M) depending on concentration. The condensation of the neutral precursor $[WO(OH)_4(OH_2)]^0$ at the PZC actually leads to the formation of layered hydrated oxides $WO_3 \cdot nH_2O$ ($n = 1$ or 2). Such precipitates are not convenient for the deposition of transparent electrochromic films. Therefore condensation reactions have to be partially prevented by adding some organic solvent such as ethanol or DMSO (dimethylsulfoxide) [29,30].

The best way to stabilize aqueous solutions of W^{VI} precursors is to use complexing reagents such as hydrogen peroxide. Stable solutions of peroxotungstic acid can be

easily obtained via the digestion of tungsten, tungsten carbide or even tungsten oxide by an aqueous solution of hydrogen peroxide [15,31–33]. A peroxotungstic acid $[WO_2(O_2)H_2O]\cdot nH_2O$ is formed in which two OH groups are replaced by one peroxo anion $[O_2]^{2-}$ that behaves as a chelating ligand preventing further condensation [35]. This peroxotungstic acid can be dissolved in a mixture of alcohol and carboxylic acids for deposition [36,37]. It is decomposed into WO_3 upon heating the film around 200°C [38].

MoO_3 layers can be deposited from alkoxides [39], chlorides [40], chloro-alkoxides [41,42] or molybdic acid [43]. However their electrochromic properties are not as good as those of WO_3 and very few papers report on MoO_3 EC coatings. Pure MoO_3 and mixed MoO_3-WO_3 or MoO_3-V_2O_5 coatings can be also formed via the peroxo route. They have been reported to exhibit excellent electrochromic properties after heat treatment at 120°C [44–46].

3.2. *Pentavalent oxides, V_2O_5 and Nb_2O_5*

The electrochemical insertion of Li^+ ions in vanadium pentoxide is highly reversible and V_2O_5 is a good candidate as a positive electrode in lithium batteries [47]. It can also be used as an electrochromic layer but the change in coloration is not very strong. Therefore it is used mainly as a counter electrode for ion storage in conjunction with WO_3.

Vanadium alkoxides are not very sensitive toward hydrolysis and the sol–gel synthesis of oxide layers is quite easy to perform [48,49]. Bulky alkoxy groups such as iso-propoxide $VO(OPr^i)_3$ or tertio-amyl $VO(OAm^t)_3$ are usually chosen in order to decrease the reactivity of the alkoxide. More stable solutions can be obtained when acetic acid or acetylacetone is added to the alkoxide precursor. These bidentate ligands form complexes with the metal atom increasing its coordination [16,49]. Alkoxyhalides of vanadium synthesized via the dissolution of VOX_3 (X = F, Cl, Br) in alcohol have also been used to form electrochromic coatings [40].

Vanadium pentoxide can also be deposited from aqueous $V_2O_5\cdot nH_2O$ sols or gels. However, because of the viscosity of the gels, the coatings are rather thick and no longer transparent. Such layers would find application as cathodes for batteries rather than for optical devices [47].

As shown by Kudo et al. vanadium oxide gels can also be obtained via the reaction of V_2O_5, vanadium metal or vanadium carbide with H_2O_2 [51,52]. Peroxo complexes of V^v are much less stable than similar complexes formed with W^{VI}, presumably because of the catalytic properties of V_2O_5. They slowly decompose giving a decavanadic acid $H_6V_{10}O_{28}$ that polymerizes into polyvanadic acid gels. A layered hydrated vanadium oxide $V_2O_5\cdot nH_2O$ is formed upon drying [53].

$Nb(OR)_5$ alkoxides are quite expensive and highly sensitive to moisture. They have to be stabilized by adding acetic acid in order to get stable sols [54]. Therefore chloro-alkoxides formed via the dissolution of $NbCl_5$ in EtOH are easier to use [55–57]. Amorphous layers are formed at room temperature. They turn to a gray-brown color upon electrochemical reduction. A crystalline oxide is formed upon heating above 400°C that turns to dark blue upon electrochemical reduction [58].

Aqueous solutions of peroxo-polyniobic acid have also been used for the deposition of Nb_2O_5 layers [59].

3.3. Tetravalent oxides, TiO_2, CeO_2 and IrO_2

TiO_2 turns gray when reduced by Li^+ ions. However its coloration is not very strong and this oxide is generally not used alone in electrochromic devices. It can be mixed with WO_3 or V_2O_5 to improve their durability or with CeO_2 for making ion storage layers.

TiO_2 coatings can be easily deposited from alkoxide solutions [60–63]. The best precursor seems to be $Ti(OBu^n)_4$ that despite the steric hindrance of the Bu^n group still exhibits an oligomeric molecular structure. It is therefore not too sensitive to moisture and can be handled easily. Complexing reagents such as acetic acid can also be added to prevent precipitation [49]. The alcoholic solution is deposited via spin or dip-coating and hydrolysis is performed by the ambient moisture. An amorphous coating is obtained that crystallizes into anatase upon heating at 400°C. The colored state of pure TiO_2 coatings is gray, but it can turn to blue upon doping with Al or Cr [50].

CeO_2-TiO_2 coatings appear to exhibit good properties as optically passive counter electrode for ion storage. Cerium exhibits two valence states Ce^{III} and Ce^{IV} but remains transparent in the visible range. $Ce(OBu^n)_4$ can be mixed with $Ti(OR)_4$ ($R = Bu^n$ or Pr^i) [65] but cerium alkoxides are not easy to make and inorganic precursors such as $Ce(NH_4)_2(NO_3)_6$ [65–69], cerium chloride $CeCl_3$ [70,71] or cerium nitrate $Ce(NO_3)_3$ [72] seem to be more convenient.

The electrochromic iridium oxide is actually a hydrous oxide rather than the crystalline IrO_2. Thin films have been deposited by a variety of techniques, but very few papers have reported sol–gel methods. Actually iridium alkoxides would be very difficult to synthesize and therefore, precursor solutions are mainly based on $IrCl_3 \cdot 3H_2O$ dissolved in water [73] or isopropanol [74].

3.4. Trivalent oxides, Fe_2O_3

The electrochemical properties of iron oxide thin films have been reported recently. They can be deposited from alkoxides [75]. Typically iron iso-propoxide in isopropanol is stabilized by triethanolamine as a complexing additive. The solution is spin-coated, left in air for hydrolysis and heated at 250°C leading to amorphous Fe_2O_3. These films exhibit good optical quality and reversible lithiation insertion, but their cathodic coloration is rather weak [76]. Inorganic precursors such as $Fe(NO_3)_3$ or $FeCl_3$ have also been used. They give precipitates rather than sols and have to be peptized with acetic acid [77].

3.5. Divalent oxides, NiO

Nickel oxide exhibits anodic electrochromism and can be used as a complementary electrode with WO_3. NiO changes from a colorless state to a brown colored

oxy-hydroxide upon electrochemical oxidation:

$$NiO + xOH^- \Leftrightarrow NiO(OH)_x + xe^-.$$

However because of coordination expansion, nickel alkoxides $Ni(OR)_2$ tend to polymerize into insoluble precursors. Therefore very bulky organic ligands such as 2-methoxyethoxide have to be used to prevent oligomerization [78].

4. Electrochromic sol–gel devices

4.1. Device materials: Chemical systems

A conventional and most studied design of an electrochromic device is a 5-segment design covered on two sides by glass substrates (Fig. 1)

glass/TCO/EC/E/IS/TCO/glass

The segments are:

(i) Two transparent conducting (TCO) oxide layers. The material is typically indium–tin oxide (ITO) or fluorine-doped tin oxide (FTO) deposited by sputtering or CVD process and has a sheet resistance commonly around $10\,\Omega/\square$. Such coatings are commercially available on both glass (ITO, FTO) and plastic substrates (ITO). They can also be made via wet chemistry, but although the optical properties are excellent, the electrical properties of sol–gel deposited coatings are not as good as those of commercial materials. Therefore little work has been done on sol–gel-deposited electronic or ionic conductive coatings for EC applications [61,78,79].

(ii) An electrochromic (EC) layer. This is typically a transition metal oxide that can exhibit several valence states upon reduction. The coloration results from electron delocalization between these mixed valence states. Hexavalent tungsten oxide in thin film form has been found to exhibit the most promising coloration/bleaching characteristics [5,6] from transparent or light yellow to deep blue on insertion of Li^+ or H^+ in the structure and back to the "colorless" state on extraction of the ion (reduction/oxidation reaction) as a function of a repeated voltage sweep (say, around -1.5 to $+1.5$ V):

$$\underset{\text{white}}{WO_3} + xM^+ + xe^- \Leftrightarrow \underset{\text{blue}}{M_xWO_3} \quad (M^+ = Li^+ \text{ or } H^+). \tag{10}$$

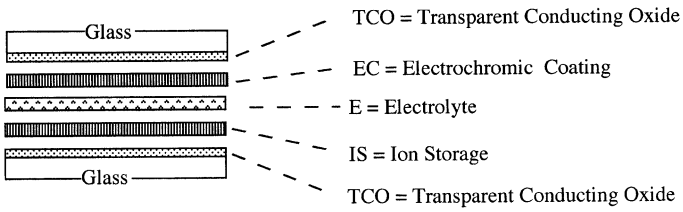

Fig. 1. Typical 5-segments electrochromic device.

Table 1
Sol–gel cathodic and anodic electrochromic films

Materials	References (see also Refs. [5,7,8])	Coloration
WO_3	[16–37]	Cathodic
WO_3–TiO_2	[86–89]	Cathodic
WO_3–V_2O_5	[90]	Cathodic
MoO_3	[44–46]	Cathodic
Nb_2O_5	[54–59]	Cathodic
TiO_2	[48,60–63]	Cathodic
Fe_2O_3	[76]	Cathodic
Fe_2O_3-TiO_2	[107]	Cathodic
V_2O_5	[40,47–53]	Cathodic/anodic
V_2O–TiO_2	[95,96]	Cathodic/anodic
$Co(OH)_2$	[100]	Anodic
Co_3O_4	[78,106]	Anodic
$IrO_2 \cdot nH_2O$	[73,74]	Anodic
$NiO \cdot nH_2O$	[101,105]	Anodic

These films show better efficiency when amorphous, and when containing low water of hydration. Table 1 provides a list of known electrochromic materials obtained in thin-film form by sol–gel processing.

(iii) An ion storage (IC) layer, which can also show coloration/bleaching properties on insertion/extraction of ions. However, it is apparently suitable for IC films to be optically passive, so as to avoid interference with the EC film coloration. The other option is to have a cathodic EC and an anodic electrochromic IS so that both coatings color and bleach at the same time. Sol–gel films of V_2O_5, TiO_2, $TiO_2^-CeO_2$, etc. have been used for ion storage. However, there are instances where laboratory sol–gel devices have been fabricated without an IS film but using a suitable electrolyte [61]. Sol–gel-derived IS films, which may also have coloration/bleaching properties, are also listed in Table 1.

(iv) An electrolyte (E) at the center, in contact with both (EC) and (IC). The electrolyte used, in early devices and for measurement of coloration/bleaching and current/voltage characteristics as a function of voltage sweep (cyclic voltammetry) is a liquid or a "semi-solid" (e.g. H_2SO_4 solution for proton conduction and propylene carbonate with $LiClO_4$ for Li^+ conduction) [80]. The inherent advantage of high diffusion rates of ions through fluids seems to be the motivation behind this. However, it was appreciated before long that leakage of the liquid or liquid-like electrolyte and damage of the EC or IS layer lead to early failure of devices. Consequently, solid electrolytes became the choice, while liquids are still being used for cycling laboratory studies. Sol–gel-derived and polymeric solid or semi-solid electrolytes of different kinds are now used in experimental electrochromic devices. Table 2 lists examples of electrolytes in experimental cells or devices.

Some hybrid organic–inorganic sol–gel materials have been suggested as electrolytes in EC devices. "Aminosils" are obtained from $H_2NSi(OR)_3$ precursors

Table 2
Electrolytes used in sol–gel electrochromic cells and devices

Electrolyte system	Ref.
Li^+ conduction	
$LiClO_4$ in propylene carbonate	[16,26,47,76,90,91,93,96,97,100]
$LiClO_4$ in polyethylene oxide [$P(EO)_8$]	[102]
$LiNbO_3$	[99]
$LiClO_4$ in acetonitrile	[56]
LiCl/LiI in polyvinyl butyral resin	[61]
LiTf (lithium triflate) in polyethylene glycol (3PEG 5000)	[98]
LiN (SO_2CF_3) in polyethylene oxide	[65]
proton conduction	
H_2SO_4	[83,103]
H_2SO_4/ethylene glycol	[104]
HCl	[17]
Formic acid	[103]
Ormolytes	[9,10,72]
TiO_2	[67]
Ta_2O_5	[83,84]
LiOH	[105,106]

hydrolyzed in the presence of strong mineral acids such as $HClO_4$ or HCF_3SO_3 [64]. The silica backbone provides mechanical strength while amino groups and acid provide proton conduction [81]. All gel electrochromic devices have been made using hybrid gels made from $Ti(OBu^n)_4$, acetic acid and glycerol as a proton conducting electrolyte [82].

Hydrous oxides could also be used as solid-state proton conductors. Amorphous Ta_2O_5 multi-layers have been dip-coated from $Ta(OEt)_5$, using acetic acid or H_2O_2 as a stabilizer [59]. An hydrated oxide layer, $Ta_2O_5 \cdot nH_2O$, is formed that exhibits reversible proton insertion and could have promising application as proton conductors in EC devices [83,84].

4.2. *Device materials*: *Desired and obtained characteristics*

Before we examine the performance of the components of a partial or all-sol–gel 5-layer EC device, individually or collectively, we briefly discuss what performance is expected from them in some applications. For example, for a glass roof in automobiles [3,5], the so-called "sunroof" or "moonroof", some overall performance ranges are given in Table 3. A commercial all-solid electrochromic device [4] on insulating (double glazed) glass units for architectural windows offers characteristics given in Table 4. Interior automotive electrochromic mirrors are expected to withstand 30,000 cycles at $-20^\circ C$ and 30,000–40,000 cycles at 50–25°C, respectively [2].

Based on this partial account of expectations, attempts are made below to examine the obtained performances of sol–gel EC components and devices.

Table 3
Expected performance of electrochromic devices in glass roofs of automobiles [3,5]

Visible transmission	Bleached 41–70%
	Colored 15–0%
IR reflection	Bleached 20–10%
	Colored > 70%
Response time	< 15 min, but preferably < 2 min
Cycling lifetime	At least $> 2 \times 10^4$ but preferably $> 10^5$
Shelf lifetime	> 5 years, preferably 10 years
Operating temperature	Preferably — 40–100°C

Table 4
Performance parameters of a commercial EC insulating glass unit [4]

	Bleached	Darkened
Photopic transmission	55%	8%
(with range)	($\pm$ 1.5%)	($\pm$ 0.5%)
Shading coefficient	0.48	0.12
UV transmission	1.5%	0.6%

4.2.1. Electrochromic and ion storage layers

Hydrated tungsten oxides $WO_3 \cdot nH_2O$ (amorphous or crystalline) have shown to lead to promising EC layers. They all switch from colorless to blue but their electrochromic properties strongly depend on the water content in the films as detailed below:

(i) The number of Li^+ ions injected into the EC from the electrolyte increases when the amount of water decreases [26].

(ii) There could be incomplete reversibility of Li^+ insertion/extraction during the first cycles for $n < 1$ [26].

Orel et al. [85] recorded transmittance spectra of sol–gel WO_3 on SnO_2:F-coated glass (heated at 200°C/120°C) under bleaching and coloring conditions ($\pm$ 1 V) and as a function of coating thickness (up to 600 nm). The visible transmittance in the bleached state was around 0.80 or more. Under colored condition, the transmittance was nearly zero for a 600 nm film. The authors noted a decrease in the current–voltage (*CV*) response with an appreciable decrease in the measured ion charge capacity after about 250 cycles. The stability of the *CV* response was better with films baked at a relatively high temperature (200°C), but a simultaneous decrease in the ion-storage capacity and coloration/bleaching kinetics was still observed. The reported charging/discharging time was 100 s (probably under the best conditions, i.e. after a small number of cycles).

Lee [17] has reported similar spectral characterization of an alkoxide-derived, 200°C-heated film on glass, though the spectra showed transmission peaks,

apparently due to interference effects. When coated on ITO-coated glass, these films showed reduced transmittance (≈ 0.6 at 550 nm) in the bleached state. In the colored state (H^+ insertion through HCl solution), the transmittance decreased to 0.2–0.4 (deep blue within 10 s).

Optical density measurements of peroxotungstic acid-based WO_3 films on ITO-coated glass showed that films baked at 240°C (as compared to 120°C) showed improved coloration/bleaching after a few thousand cycles [72]. The response time also decreased correspondingly from about 95 to 40 s (coloration) and from 190 to 90 s (bleaching).

Vroon et al. [16] showed that alkoxide-derived WO_3 films had better coloration/bleaching difference when baked at 150–250°C (after the 4th cycle). The coloration efficiency was also better for such films.

It has been shown in recent work [86,87] that doping of WO_3 films with titanium improves the electrochromic stability. Such coatings can be easily prepared by mixing alkoxide solutions [88]. Ozer and Dogan [89] have shown that 5 mol% Ti in WO_3, baked at 150°C, had the best overall properties and a neutral grayish blue color, more suitable than blue for windows. Performance of the doped films over 1000 cycles has not been reported. Livage and Guzman reported a stability of more than 10^5 cycles (-1.5, $+1.5$ V) of a 5% TiO_2 film under lithium insertion/extraction [26]. Ozer and Lampert [90] have reported electrochromic WO_3 coatings with up to 10 mol% V_2O_5. These amorphous films of 250–300 nm thickness show somewhat larger difference in coloration-bleaching transmission compared to that of pure WO_3. The best result was obtained with 3.5 mol% V_2O_5.

A promising electrochromic material is Nb_2O_5, though apparently not so much used for fabrication of devices. Lee and Crayston [55] were probably the first to report sol–gel Nb_2O_5 films for electrochromic applications. Though these films show shrinkage-related defects, they exhibit a blue coloration with a response time of ≈ 6 s and a bleaching time of ≈ 3 s through Li^+ insertion and extraction. However, the poor durability of the electrochromic behavior of these films posed a problem. Faria and Bulhoes [56] produced films showing change in transmission from 82% to 30% (632 nm) on Li^+ insertion. Ozer et al. [91] reported niobia films showing 40% change in color from colorless to brown up to at least 1200 cycles without change in performance.

Aegerter et al. reported extensive work on the development of electrochromic Nb_2O_5 films from alkoxides and chloroalkoxides [12,92,93]. Amorphous coatings exhibit a gray-brown color. Crystalline films showed deep blue coloration on lithium insertion, but the extraction seemed to be incomplete, so that the "bleached" films were slightly colored [92]. They later reported fully reversible coloration (cycle 4 to at least 100, $+2$ to -1.8 V) for films baked at 400°C/600°C [93]. The color was dependent on the baking temperature, and the thickness-dependent transmission could go down to 20% from $\approx 80\%$.

Sol–gel titania films have been well studied for their electrochromic behavior [5]. The extensive studies of Ozer et al. deserve mention [49,94]. They reported high (90–92%) transmission of amorphous TiO_2 films in the bleached state and a gray color on insertion of Li^+ ions at -2 V within about 40 s. Reproducibility studies on

these films showed them to be very promising EC material [94]. A very interesting development is films of TiO_2–CeO_2, prepared by sol–gel processing. The first report came from Baudry et al. , who prepared almost colorless films (Ti/Ce = 1) showing attractive Li^+ insertion/extraction properties without significant change in color, and recommended them as an IS layer (counter-electrode) in devices. In a later communication, Ozer et al. [69] reported no degradation of the films or fall in their charge capacity up to 25000 cycles between -1.1 and $+0.4$ V.

Vanadium pentoxide (V_2O_5) is another extensively studied electrochromic material, known for its weakly coloring ion insertion /extraction behavior, and hence, also suitable as an IS layer. Livage et al. have reported pioneering work on sol–gel-derived films of V_2O_5 and their electrochromic characteristics [49]. Recently, Livage has summarized the sol–gel chemistry involved in the preparation of the pentoxide films and their electrochemical properties [47]. The reported color changes from yellow to green and blue could make them suitable for multicolor EC devices. A related issue is the improved reversibility reported for V_2O_5–TiO_2 films [95]. Ozer et al. [96] have shown very recently that with 5 mol% doping of Ti, the visible transmission of V_2O_5 rises by about 30%, and the drop in transmission on coloration (Li^+ insertion, -0.6–1.6 V, 10 mV/s) is nearly 20%.

The alkoxide sol–gel route has been used by Ozer for the preparation of tantalum oxide films, known for their use as proton conductors in electrochromic devices. Ozer and Lampert [90] showed from impedance plots that amorphous films showed promising proton conductivity. Recently, Tepehan et al. [83] demonstrated protonic conductivity of such films deposited on SnO_2:F/WO_3 electrode by cyclic voltammetry. Various other sol–gel electrochromic (for EC or IS) layers are listed in Table 1.

4.3. Degradation phenomena in films and devices

At least two broad factors influence the efficiency and life (durability, stability) of an EC device which are important parameters for practical applications. They are:

(i) The materials and mode of construction of the device, e.g. efficient sealing, individual stability of the chosen EC and IS layers, their interface stability with the electrolyte, operational factors, etc.
(ii) The application environment, e.g. ambient temperature range, rate of heating and cooling, effect of exposure to the ultraviolet part of the solar rays, rain, humidity and other environmental hazards [97].

While little information is apparently available on long-term testing of partial or all-sol–gel EC devices with respect to their durability and stability as a function of the application environment (indoor or outdoor), some information is indeed on record about the performance of sol–gel devices as a function of their mode of construction, including the choice of materials. The available details are discussed below.

Baker et al. [98] describe the performance of a partial sol–gel device of the type glass/ITO/WO_3/Li-triflate-polyethylene glycol/TiO_2/ITO/glass. They point out two major modes of degradation: an irreversible chemical interaction between the film and the injected ions, and a progressive decrease in structural integrity of the films. In their

device (as given above), the limited charge capacity of the TiO_2 counter-electrode and its structural degradation as a function of cycling were the cause of device degradation.

In a recent work Bell and Skryabin studied the degradation of a sealed partial sol–gel system glass/ITO/WO_3/$LiClO_4$–propylene carbonate/V_2O_5/ITO/glass [97]. After 800 cycles, both the inserted and extracted charges diminished drastically and after around 850 cycles, the device stopped functioning. This was assigned to a dissolution of the V_2O_5 counter-electrode, contaminating the electrolyte. In another similar device, the failure was assigned to the decreased performance of the WO_3 electrochromic film due to trapping of charge. It should be pointed out that the dissolution of electrodes leads to a decrease in film thickness providing undesired higher light transmittance in the colored state. Irreversible incorporation of Li^+ in WO_3 has also been reported by e.g. Munro et al. in cells [72].

It has been observed that the presence of moisture in a polymer electrolyte or its incorporation during cycling the device (e.g. due to bad sealing) can cause electrolyte failure and hence, device failure [97]. The degraded polymer can bind the conducting ion in the system and reduce charge availability. The presence of trace of water in an all-sol–gel EC device may be responsible for the poor chemical resistance of the EC film [97]. Control of water in sol–gel EC devices is thus an important factor. Orel et al. on the other hand showed that in an all-sol–gel EC devices, rapid degradation of the sol–gel ormolyte-type electrolyte takes place due to application of a large range of potentials, i.e. -4 to $+2.5$ V. This makes the potential range another factor to be considered to avoid electrolyte degradation [85].

Macedo and Aegerter described the performance of two sol–gel (except the TCO) EC devices [67]. The device glass/ITO/$TiO_2^-CeO_2$/$TiO_2^-CeO_2$/ITO/glass showed no degradation up to at least 30,000 cycles and a very fast (2.5 s) response time. However, an EC window glass/ITO/WO_3/TiO_2/TiO_2–CeO_2/ITO/glass showed a degradation in coloration within less than 400 cycles though the response time was fast (< 10 s). A suspected reason was the generation of defects in the WO_3(EC)/TiO_2 (electrolyte) interface.

5. Conclusions

Considerable research has been carried out on the development of electrochromic films by various sol–gel procedures. Many of these films show the required coloration/bleaching properties to be useful for application in devices. Several "all-gel" electrochromic devices have been described, in which all active layers are deposited from gels [34,61,67,72,82]. Further research, however, seems warranted in problems of life expectancy as a function of cycling in devices (see Table 3) and device failures due to chemical corrosion and other reasons.

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